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Nephelauxetic effects on Sm^{2+} and Eu^{3+} in ternary *MYX* compounds

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Isoelectronic Sm^{2+} and Eu^{3+} ions with their ground configuration $4f^6$ are used in different ternary *MYX* compounds to study the reduction of the Slater parameters F_k and the spin-orbit coupling parameter ζ_{4f}, commonly referred to as the nephelauxetic effect. At first, a simulation of the $4f^6$ energy levels in the intermediate coupling scheme with the two parameters F_2 and ζ_{4f} shows that the set of basis functions must include all the septets (^7L_J) and all the quintets (^5L_J), as well as some triplets (^3P_J, ^3D_J, and ^3F_J) or singlets (^1S_J, ^1P_J, and ^1D_J) to reproduce the energy level scheme accurately, whereby a strong effect of the triplets and singlets on the ^5D_J multiplets is most prominent. With structural parameters of different host materials at ambient and elevated pressures, different distance dependences of the parameters F_2 and ζ_{4f} for Sm^{2+} and Eu^{3+} are derived from the ambient-pressure and high-pressure energy-level schemes, demonstrating a breakdown of the nephelauxetic series. Only a combination of at least two microscopic covalency mechanisms, central-field covalency (CFC) and symmetry-restricted covalency (SRC), allows for a description without contradictions. Thereby the CFC contribution is dominant for the small Eu^{3+} ion, whereas the SRC is more dominant for the larger Sm^{2+} ion. Finally, *ab initio* calculations of Coulomb integrals are used to evaluate the Slater parameters F_k of Sm^{2+} within the SRC model and close agreement of these results with the experimental data is then obtained.

I. INTRODUCTION

When a lanthanide ion is incorporated into a host crystal, the so-called crystal field (CF) results in two effects, which are the CF splittings and the centroid shifts of all the free-ion multiplets. The centroid shifts are ascribed to reductions of the Slater parameters F_k and the spin-orbit coupling parameter ζ_{4f} for the lanthanide ion in the host crystal with respect to their free-ion values F_k^0 and ζ_{4f}^0 and this observation is usually referred to as the nephelauxetic effect.

Systematic considerations of the contributions of different ligands to the CF splittings and the reductions in Slater parameters for $3d$ ions resulted in two different series, respectively, the spectrochemical and nephelauxetic series. The spectrochemical series for the strength of CF splittings shows the following order:[1]

$$\text{free ion} < I^- < Br^- < Cl^- < S^{2-} < F^- < O^{2-},$$

whereas the nephelauxetic series for the centroid shifts is given[2] as

$$\text{free ion} < F^- < O^{2-} < Cl^- < Br^- < I^- \approx S^{2-}$$

and shows thus a strong anticorrelation with respect to the spectrochemical series. Newman[3] has pointed out that also $4f$ ion systems seem to follow these two series in most cases, and the large number of the CF studies on lanthanide ions in different hosts shows a strong positive correlation of the strength of overlap and covalency contributions from the crystal field. Correspondingly, various models have been proposed to explain the nephelauxetic effects either by "microscopic covalency"[4] or "macroscopic dielectric"[5] effects.

Thereby, the reduction of the free-ion parameters is usually ascribed to a $4f$ electron cloud expansion of lanthanide ions in the crystals. This expansion is modeled by two different mechanisms. Considerations of a spherically symmetric penetration from the ligand electrons are usually referred to as the central-field covalency (CFC) model and this model correlates both free-ion parameters F_k and ζ_{4f} directly with an effective nuclear charge Z_{eff} of the lanthanide ions: $F_k \sim Z_{\text{eff}}$ and $\zeta_{4f} \sim Z_{\text{eff}}^3$.[6] On the other hand, the symmetry-restricted covalency (SRC)[7] model describes the symmetry-dependent admixture of $4f$ orbitals (φ_m) with neighboring ligand orbitals (χ_τ). Within a first approximation the modified $4f$ orbitals are simply normalized as $\mathcal{N}_m\varphi_m$, so that the free-ion parameters of lanthanide ions in the crystal are obtained as $F_k \approx \mathcal{N}^4 F_k^0$ and $\zeta_{4f} \approx \mathcal{N}^2 \zeta_{4f}^0$, and the renormalization constants $\mathcal{N}_m$ are usually treated as empirical parameters.

In the macroscopic dielectric model the host crystal is considered as a dielectric continuum, which reduces the Coulomb interaction between $4f$ electrons of lanthanide ions. According to this model, the reduction of the Slater parameters is given as $\Delta F_k \sim R_S^{-(2k+1)}$, where R_S is a suitably selected value for the ionic radius of the lanthanide ion.

Recent high-pressure studies[8,9] demonstrated clearly that the relative decrease of the spin-orbit coupling parameter is much smaller than the variation of the Slater parameters. Obviously, the CFC model cannot explain this variation. The dielectric model, on the other hand, involves large uncertainties in the choice of the radius R_S, limiting its application. However, the predictions of the SRC model are at least qualitatively supported by the high-pressure results, but an earlier *ab initio* calculation[10] for Pr^{3+} in $PrCl_3$ predicted that these covalency contributions are an order of magnitude too small to account for the reduction of the Slater parameters.

By the use of all the available data for Sm^{2+} and Eu^{3+} ions in different ternary *MYX* host materials at ambient pressure together with recent high-pressure results, the present

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study attempts to resolve these discrepancies, and it is shown that the combination of the two covalency mechanisms leads to quantitatively correct results.

II. REPRESENTATION OF FREE-ION ENERGY LEVELS

The electronic ground state of the isoelectronic Sm^{2+} and Eu^{3+} ions is represented by a $4f^6$ configuration. The Coulomb interaction (H_C) splits this configuration into 119 ^{2S+1}L spectral terms and the spin-orbit coupling ($H_{s.o.}$) produces 295 $^{2S+1}L_J$ multiplets. The calculation of energy levels proceeds by a diagonalization of the free-ion Hamiltonian H_{FI},

$$\langle|H_{FI}|\rangle=\langle|H_C|\rangle+\langle|H_{s.o.}|\rangle$$
$$=\sum_k f^k F_k+\zeta_{4f}\left\langle\left|\sum_i s_i\cdot l_i\right|\right\rangle, \qquad (1)$$

with the use of a set of basis functions, where the f^k depend only on the angular parts of the electronic wave functions and are calculated therefore exactly. s_i and l_i represent the spin and orbital angular momentum of the ith $4f$ electron. The parameters F_2, F_4, F_6, and ζ_{4f} are treated as free parameters to be determined from the experimentally observed energy levels. Since the Coulomb and spin-orbit interactions are of about equal magnitude for $4f$ electron systems, the intermediate coupling scheme must be applied in the evaluation of the eigenvalues for Eq. (1).

In addition to these two most important interactions for the determination of the energy levels, there are some higher-order interactions, as, for example, the two- and three-body configuration interactions and the spin-spin interactions with contributions to the energy levels typically less than 100 cm^{-1}.

Furthermore, one can take into account that the ratios of the Slater parameters, F_4/F_2 and F_6/F_2, for all the lanthanide ions are very close to their hydrogenic values. With these fixed ratios, the energy levels depend then only on the two parameters F_2 and ζ_{4f}.

It is well known that the multiplets for the $4f^6$ configuration consist of 7 septets, 74 quintets, 168 triplets, and 46 singlets. However, for Sm^{2+} and Eu^{3+} ions in different hosts only ^7F_J and ^5D_J multiplets are usually observed by spectroscopic measurements. Thus, the set of basis functions for the 295 multiplets must be truncated in the fit of the considerably smaller experimental data sets. In the present work, three different basis sets are used to estimate the effects from the truncation on the multiplets of ^7F_J and ^5D_J.

At first, only the septets and quintets are selected as basis set 1. In order to study the contributions of the triplets and singlets to the ^7F_J and ^5D_J multiplets, the basis set 2 includes in addition 18 ^3P_J, 15 ^3D_J, and 27 ^3F_J triplets, and the basis set 3 involves furthermore 4 ^1S_J, one ^1P_J, and 6 ^1D_J singlets. The results for the ^7F_J and ^5D_J multiplets are then schematically illustrated in Fig. 1.

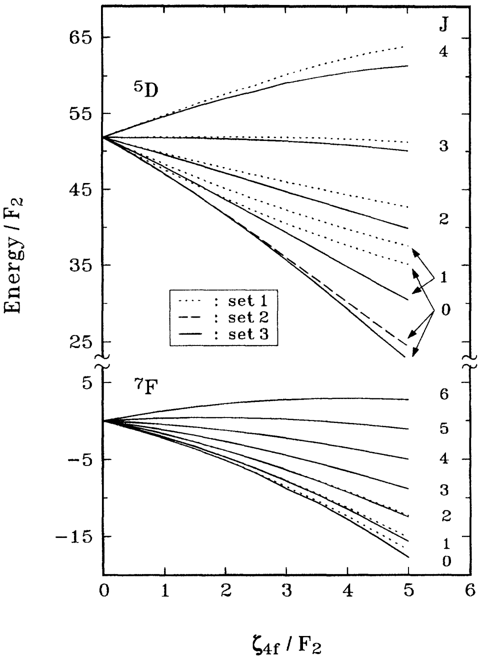

FIG. 1. Variation of the ^5D_J and ^7F_J multiplets of the $4f^6$ configuration as a function of ζ_{4f}/F_2, calculated with different basis sets discussed in the text.

Since the values of ζ_{4f}/F_2 for Sm^{2+} and Eu^{3+} ions range typically from 3 to 4, the singlets have a distinct effect on the energy position of the $^5D_0$ multiplet but only a minor influence on the other multiplets. As shown in Fig. 1, the triplet contributions to the ^5D_J mulitplets are quite important. As an example, the decomposition of the free-ion wave functions for the multiplets $^7F_0$ and $^5D_0$ are given here for $\zeta_{4f}/F_2=3.5$:

$$|^7F_0\rangle\approx 92.8\%|^7F\rangle+6.9\%|^5D\rangle+0.3\%|^3P\rangle$$

and

$$|^5D_0\rangle\approx 79\%|^5D\rangle+14\%|^3P\rangle+6\%|^7F\rangle+1\%|^1S\rangle.$$

This decomposition shows that the ground multiplet $^7F_0$ is only marginally affected by the other multiplets and follows thus a LS coupling scheme, because all the perturbing states are just too far away. However, the ^5D_J multiplets are not only strongly affected by the triplets but also weakly by the singlets with a breakdown of the LS coupling scheme in this case. This wave function admixture explains also the observation of the "forbidden" transition $^5D_0\leftrightarrow{}^7F_0$ for Sm^{2+} and Eu^{3+} in many different hosts.

Finally, one has to estimate the contributions from the configuration interactions. If the most important term of the two-body configuration interactions, $\alpha L(L+1)$ introduced by Trees,[11] is taken into account, this leads to a change of ~0.7% for F_2 and ~0.15% for ζ_{4f}, estimated here with $\zeta_{4f}/F_2=3.5$ and $\alpha/F_2\approx 0.05$ of Eu^{3+}:$LaCl_3$.[12]

III. EXPERIMENTAL RESULTS FOR THE FREE-ION PARAMETERS

Experimental data on multiplets for the evaluation of the free-ion parameters F_2 and ζ_{4f} are available for Sm^{2+}:MFCl (M = Ba, Sr, and Ca), Eu^{3+}:$LO\ X$ (L = La, Gd, or Y and X = Cl, Br, or I),[13,14] and Eu^{3+}:L_2O_2S (L =

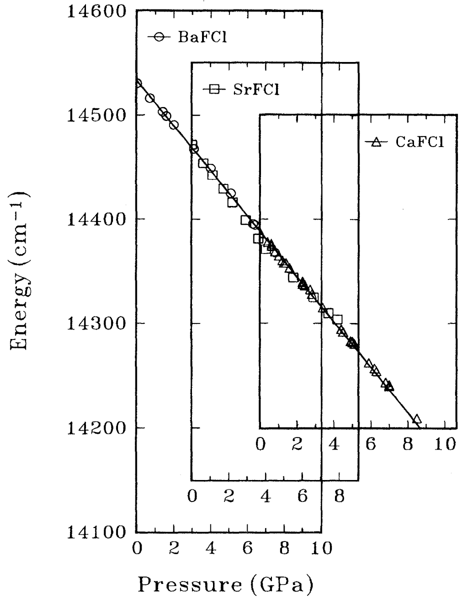

FIG. 2. Variation of the $^5D_0$ multiplets for Sm^{2+}:*M*FCl under pressure. The data for Sm^{2+}:SrFCl and for Sm^{2+}:CaFCl are shifted with respect to Sm^{2+}:BaFCl by pressures of 3 GPa and 6.7 GPa, respectively.

La, Gd, Y, and Lu) (Ref. 15) at ambient pressure as well as for Eu^{3+}:LaOCl (Ref. 16) and Eu^{3+}:LaOBr (Ref. 17) at room temperature under pressures up to 13 GPa and for Sm^{2+}:*M*FCl at 20 K under pressures up to 8 GPa. While all the results for $^7F_{0-6}$ multiplets of Sm^{2+}:*M*FCl were reported in previous studies,[18–20] additional information on three ^5D_J multiplets, $^5D_{0-2}$, was obtained in this study with the result that the rates of pressure-induced shifts for their centroids have the same values of -21 cm^{-1}/GPa, -24 cm^{-1}/GPa, and -29 cm^{-1}/GPa, respectively, in the three different hosts. As an example, the variation of $^5D_0$ for Sm^{2+}:*M*FCl under pressure is shown in Fig. 2, where the data for Sm^{2+}:SrFCl and Sm^{2+}:CaFCl are shifted with respect to Sm^{2+}:BaFCl by pressures of 3 GPa and 6.7 GPa, respectively. The same behavior is noticed also for $^5D_1$ and $^5D_2$.

The parameters F_2 and ζ_{4f} are then obtained by least squares fitting with respect to the observed multiplet centroids. In the cases where the complete CF levels of some multiplets could not be observed experimentally to determine their centroids, the missing CF levels were calculated first by the use of a CF fitting, including also *J* mixing effects, and these missing values for the CF levels of the multiplets are then added to the experimental values in the final determination of these centroids.

A. Free-ion parameters at ambient pressure

A hydrogenic approximation for the set of basis functions in Eq. (1) results by the use of a least squares fitting procedure in the values of the parameters F_2 and ζ_{4f} for Sm^{2+} ions given in Table I, which shows a remarkably good agreement between fitted and experimental energy levels by standard deviations σ around 10 cm^{-1}.

TABLE I. Free-ion parameters F_2 and ζ_{4f} (in cm^{-1}) for Sm^{2+} and Eu^{3+} in different hosts at ambient pressure with standard deviations in parentheses. The numbers of multiplets used in the fits are 10 for Sm^{2+}, 8 for Eu^{3+}:*LOX*, and 9 for Eu^{3+}:L_2O_2S. σ (cm^{-1}) denotes the standard deviations between observed and calculated energy levels. The experimental data for the multiplets of Eu^{3+} are taken from Refs. 13, 14, and 15, respectively.

Sample	F_2	ζ_{4f}	σ
Sm^{2+}:BaFCl	332.0(2)	1058(2)	13.0
Sm^{2+}:SrFCl	330.7(2)	1057(2)	10.0
Sm^{2+}:CaFCl	328.8(1)	1055(1)	6.7
Eu^{3+}:LaOCl	384.3(3)	1348(3)	15.9
Eu^{3+}:GdOCl	383.0(2)	1336(2)	8.1
Eu^{3+}:YOCl	382.7(2)	1334(2)	10.4
Eu^{3+}:LaOBr	384.8(3)	1356(4)	17.8
Eu^{3+}:GdOBr	383.2(2)	1339(2)	8.1
Eu^{3+}:YOBr	382.9(2)	1337(2)	7.4
Eu^{3+}:LaOI	384.5(3)	1353(4)	17.2
Eu^{3+}: La_2O_2S	382.3(3)	1327(4)	17.5
Eu^{3+}: Gd_2O_2S	381.6(3)	1325(4)	15.7
Eu^{3+}: Y_2O_2S	381.4(2)	1325(3)	15.3
Eu^{3+}: Lu_2O_2S	381.1(2)	1324(3)	15.0

For Eu^{3+} ions the fitting in the hydrogenic approximation leads also to a reasonable agreement with the experimental data, however, with slightly larger standard deviations of $\bar{\sigma}\sim$ 20 cm^{-1} in comparison with the cases of Sm^{2+} ions with $\bar{\sigma}$ = 10 cm^{-1}. These larger deviations are possibly due to the hydrogenic approximation. In fact, it has been noticed previously in an evaluation of the free-ion parameters for all the trivalent lanthanide ions in $LaCl_3$ that the average values for the ratios $F_4/F_2=0.148(4)$ and $F_6/F_2=0.016(1)$ (Ref. 12) show close agreement with the hydrogenic value of 0.0151 in the latter case, whereas the hydrogenic value of 0.138 for F_4/F_2 deviates slightly from the best fitted value. Similarly, it is noticed in the present fits that the use of the "experimental" F_4/F_2 ratio from $LaCl_3$ improves also the present results. For example, the deviation of $\sigma=21.4$ cm^{-1} for Eu^{3+}:GdOCl is reduced to $\sigma=8.1$ cm^{-1} by the use of the "experimental" ratio $F_4/F_2=0.148$, and therefore, this ratio is used in the fitting procedure for the evaluation of the parameters F_2 and ζ_{4f} for Eu^{3+} presented in Table I. Corresponding observed and calculated energy levels for Sm^{2+}:SrFCl, Eu^{3+}:GdOCl, and Eu^{3+}:Gd_2O_2S are listed in Table II just as typical examples.

The results in Tables I and II indicate clearly that the two-parameter set can reasonably describe the energy-level schemes for Sm^{2+} and Eu^{3+} ions in their $4f^6$ configurations. Previously, Ofelt[21] has studied these $4f^6$ configuration systems, but without taking into account the influence of the singlets with the results $F_2=330$ cm^{-1} and $\zeta_{4f}=1050$ cm^{-1} for Sm^{2+} and $F_2=401$ cm^{-1} and $\zeta_{4f}=1320$ cm^{-1} for Eu^{3+}. These data give reductions for F_2 and ζ_{4f} of -18% and -20% from Eu^{3+} to Sm^{2+}, whereas the present study gives average reductions of $-14(1)\%$ for F_2 and $-21(1)\%$ for ζ_{4f} from the data in Table I.

TABLE II. Observed and calculated energy levels (cm^{-1}) for Sm^{2+}:SrFCl, Eu^{3+}:GdOCl, and Eu^{3+}:Gd_2O_2S at ambient pressure. Only for the comparison with the calculated values also the estimated values for incomplete CF levels are given in parentheses.

	Sm^{2+}:SrFCl		Eu^{3+}:GdOCl		Eu^{3+}: Gd_2O_2S	
Multiplet	E_{obs}	E_{cal}	E_{obs}	E_{cal}	E_{obs}	E_{cal}
$^7F_0$	0	0	0	0	0	0
$^7F_1$	285	293	379	386	360	381
$^7F_2$	809	813	1065	1061	1032	1050
$^7F_3$	1486	1491	1932	1932	1910	1912
$^7F_4$	2269	2274	2914	2927	2882	2899
$^7F_5$	3124	3126	(4000)	4000	(3915)	3963
$^7F_6$	4014	4022	–	5188	(4988)	5073
$^5D_0$	14472	14495	17217	17231	17155	17182
$^5D_1$	15804	15794	18976	18966	18910	18898
$^5D_2$	17734	17721	21444	21440	21370	21351
$^5D_3$	–	20040	(24337)	24353	24239	24242
$^5D_4$	–	22715	(27624)	27662	–	27526

At this point, some comments on the literature data seem to be appropriate.

(i) For Sm^{2+} in *M*FCl the value for ζ_{4f} was deduced only from the 7 ^7F_J multiplets with the results of 1154 cm^{-1} for Sm^{2+}:BaFCl (Ref. 22) and 1361 cm^{-1} for Sm^{2+}:SrFCl.[23] These larger values in comparison with the present results can be traced back to the neglection of the intermediate coupling. If only the ^7F_J multiplets would be used also here, a value of ζ_{4f} = 1056 cm^{-1} would be obtained for Sm^{2+}:SrFCl. This observation illustrates that the value for ζ_{4f} is clearly affected by the intermediate coupling, even if the wave functions for the ^7F_J multiplets are dominated by more than 90% by the contributions from the *LS* components.

(ii) Attempts by Hölsä and Porcher[13,14] to fit the observed energy levels of Eu^{3+}:*LOX* resulted in standard deviations σ from 29 to 39 cm^{-1} for *L*OCl and from 28 to 45 cm^{-1} for *L*OBr and did not show any systematic variation of either F_k and ζ_{4f} within this class of isostructural crystals. A new attempt[24] with smaller basis sets gave no improvements. One can thus conclude that not only the intermediate coupling but also extended basis sets are needed to describe in this case the $4f^6$ configuration accurately.

B. Pressure dependence of free-ion parameters

When the same procedures are used to derive the pressure dependence of the parameters F_2 and ζ_{4f} from the high-pressure data of Sm^{2+}:*M*FCl up to 8 GPa, of Eu^{3+}:LaOCl, and Eu^{3+}:LaOBr up to 13 GPa, one finds that the standard deviations decrease with increasing pressure almost by a factor of 2 in all the cases except for Sm^{2+}:CaFCl. This overall decrease in σ results mainly from better fits of the ^5D_J multiplets.

A simple explanation of this effect cannot be found in the literature. Some hints are given, however, by the observation that higher-order interactions for instance in the form of correlation crystal fields[25] (CCF's) affect the CF splittings of the ^5D_J multiplets for Sm^{2+} and Eu^{3+},[18] in a similar way in the case of $^2H_{11/2}$ for Nd^{3+}.[26] High-pressure studies on Nd^{3+}:$LaCl_3$ (Ref. 27) lead to the interesting result that the influence of the CCF effects on the $^2H_{11/2}$ splittings shows a strong decrease under pressure, and a similar mechanism may apply also in the present case.

The variations of F_2 and ζ_{4f} under pressure are illustrated in Figs. 3–6 with the same pressure shifts of the frames applied already in Fig. 2 and with a pressure shift of 3.3 GPa

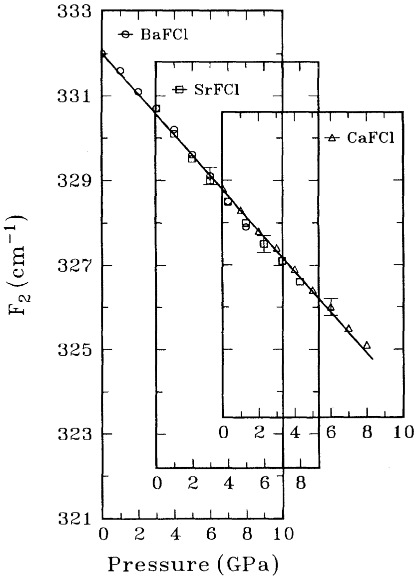

FIG. 3. Variation of the parameter F_2 for Sm^{2+}:*M*FCl under pressure. The data for Sm^{2+}:SrFCl and for Sm^{2+}:CaFCl are shifted with respect to Sm^{2+}:BaFCl by pressures of 3 GPa and 6.7 GPa, respectively.

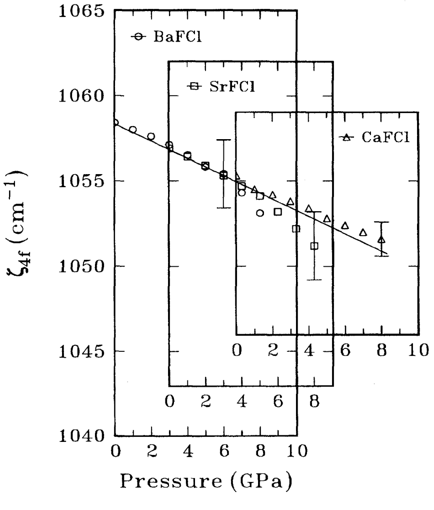

FIG. 4. Variation of the parameter ζ_{4f} for Sm^{2+}:*M*FCl under pressure. The data for Sm^{2+}:SrFCl and for Sm^{2+}:CaFCl are shifted with respect to Sm^{2+}:BaFCl by pressures of 3 GPa and 6.7 GPa, respectively.

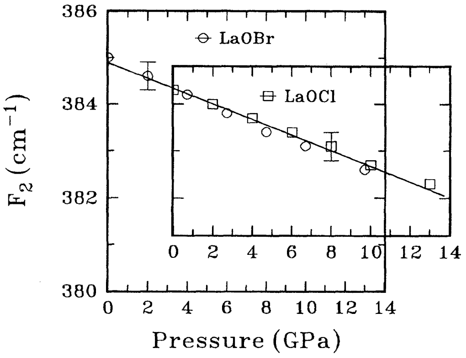

FIG. 5. Variation of the parameter F_2 for Eu^{3+}:LaOCl and Eu^{3+}:LaOBr under pressure. The data for Eu^{3+}:LaOCl are shifted with respect to Eu^{3+}:LaOBr by a pressure of 3.3 GPa.

for Eu^{3+}:LaOCl with respect to Eu^{3+}:LaOBr. In all these cases, a linear pressure dependence is observed with slopes for F_2 of $-0.482(6)$ cm^{-1}/GPa for Sm^{2+} and of $-0.167(6)$ cm^{-1}/GPa for Eu^{3+}, and for ζ_{4f} of $-0.51(3)$ cm^{-1}/GPa for Sm^{2+} and of $-1.23(6)$ cm^{-1}/GPa for Eu^{3+}.

Evidently, the pressure-induced change of the Slater parameter F_2 for Sm^{2+} is about 3 times as strong as for Eu^{3+}, whereas the spin-orbit parameter ζ_{4f} of Sm^{2+} shows only about half the shift of Eu^{3+}.

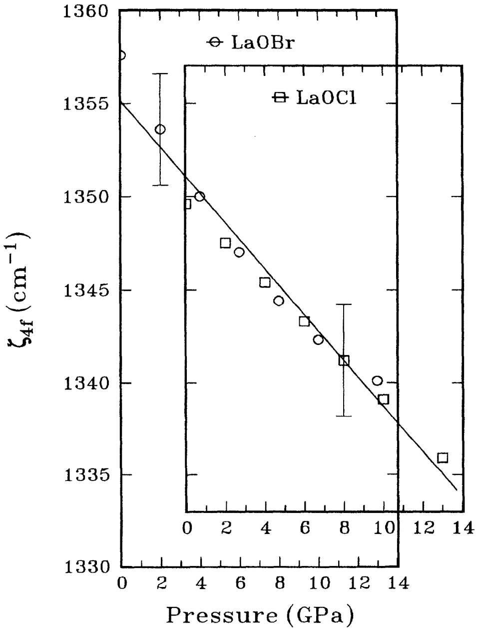

FIG. 6. Variation of the parameter ζ_{4f} for Eu^{3+}:LaOCl and Eu^{3+}:LaOBr under pressure. The data for Eu^{3+}:LaOCl are shifted with respect to Eu^{3+}:LaOBr by a pressure of 3.3 GPa.

IV. DISCUSSIONS

A. Distance dependence of free-ion parameters

A deeper understanding of the nephelauxetic effects on Sm^{2+} and Eu^{3+} ions not only in different hosts at ambient conditions but also under pressure requires an analysis on the basis of interionic distances.

Ternary MYX compounds of the type MFX, LOX, and L_2O_2S were considered as host materials for Sm^{2+} and Eu^{3+} ions, whereby both the MFX and LOX compounds belong to a tetragonal PbFCl-type structure and the L_2O_2S compounds to a hexagonal structure. In the PbFCl-type structure, M or L cations are coordinated by nine ligands, four F or O anions at R_1, four X anions at R_2, and an extra X anion located at R_3 on the crystallographic axis c. In the hexagonal structure of L_2O_2S, L cations are surrounded by three S anions at R_1, three O anions at R_2, and an extra O anion at R_3. The interionic distances R_i and the coordination numbers n_i of the first-nearest-neighboring ligands are given in Table III together with an average distance for the coordination polyhedra $\bar{R}=\Sigma n_i R_i/\Sigma n_i$.

The dependence of the parameters F_2 and ζ_{4f} on $\bar{R}$ is represented in Figs. 7 and 8, where the effects of pressure for Sm^{2+}:MFCl and Eu^{3+}:LaOCl are shown by solid arrows. The variations of the distances under pressure for MFCl hosts are given in the literature.[18,19] For LaOCl, reasonable estimates could be made by assuming constant values for the atom position parameters z_{La} and z_{Cl} under pressure together with experimental data for the host lattice parameters a and c.[35]

As shown in Figs. 7 and 8, F_2 and ζ_{4f} decrease almost linearly with decreasing interionic distances; however, the pressure-induced decrease in F_2 and ζ_{4f} shows significant deviations from the host-induced shifts. To a large extent, these deviations are accounted for by local distortions around the lanthanide ions in the different host crystals due to the different ionic size of the host lattice cations with respect to the impurity ions. For example, the Sm^{2+} ions in the three different MFCl hosts have negligible distortions in SrFCl due to the same ionic size of Sm^{2+} and Sr^{2+}; however, negative distortions are expected in BaFCl due to the larger ionic size of Ba^{2+} with respect to Sm^{2+}, and positive distortions must be taken into account in CaFCl due to the smaller ionic size of Ca^{2+}. As shown in Fig. 2, the ^5D_J-multiplet centroid positions, expanded by -3 GPa for Sm^{2+} in BaFCl and contracted by 3.7 GPa for Sm^{2+} in CaFCl with respect to Sm^{2+} in SrFCl, coincide with each other at ambient conditions and show then under pressure also the same shifts. If one assumes that all the multiplet centroid shifts of Sm^{2+} in different isostructural crystals are energetically similar, the local structures around Sm^{2+} in these crystals result in identical shifts. The same approach leads also to a consistent picture for both F_2 and ζ_{4f} of Sm^{2+}: MFCl as shown in Figs. 3 and 4. In any case, one obtains direct informations on local structures around the lanthanide ions in different isostructural crystals, when one compares the ambient-pressure data with high pressure results.

Furthermore, Figs. 7 and 8 show very clearly that the decrease in both F_2 and ζ_{4f} for Eu^{3+} in the host series LaOI-LaOBr-LaOCl, GdOBr-GdOCl, and YOBr-YOCl is reversed with respect to the nephelauxetic series of ligands. Also in

TABLE III. Interionic distances R (pm) of the nearest ligands. $\bar{R}$ (pm) represents an average distance (see text) and n denotes the number of ligands in the coordination polyhedron. The values of $\bar{R}$ marked by an asterisk are calculated for the eight nearest neighbors only, because the contribution of the ninth ion is relatively small in the case of LaOI, GdOBr, and YOBr.

Crystal	n	Ligand	R (pm)	$\bar{R}$ (pm)	Ref.
	4	F	264.9		
BaFCl	4	Cl	328.6	299.3	28
	1	Cl	319.6		
	4	F	249.4		
SrFCl	4	Cl	311.2	283.3	28
	1	Cl	307.2		
	4	F	236.2		
CaFCl	4	Cl	296.3	270.5	29
	1	Cl	304.8		
	4	O	238.7		
LaOCl	4	Cl	320.5	283.3	30
	1	Cl	312.6		
	4	O	240.0		
LaOBr	4	Br	328.0	291.0	31
	1	Br	347.0		
	4	O	241.0		
LaOI	4	I	348.0	294.5*	31
	1	I	479.0		
	4	O	228.4		
GdOCl	4	Cl	309.8	272.9	32
	1	Cl	303.6		
	4	O	228.0		
GdOBr	4	Br	320.0	274.0*	33
	1	Br	390.0		
	4	O	228.4		
YOCl	4	Cl	300.4	268.7	31
	1	Cl	303.5		
	4	O	228.0		
YOBr	4	Br	318.0	273.0*	33
	1	Br	396.0		
	3	O	242.3		
La_2O_2S	1	O	242.4	268.6	34
	3	S	303.7		
	3	O	227.2		
Gd_2O_2S	1	O	233.3	257.0	31
	3	S	294.7		
	3	O	223.0		
Y_2O_2S	1	O	229.7	252.5	31
	3	S	289.7		
	3	O	218.9		
Lu_2O_2S	1	O	227.0	248.4	31
	3	S	285.0		

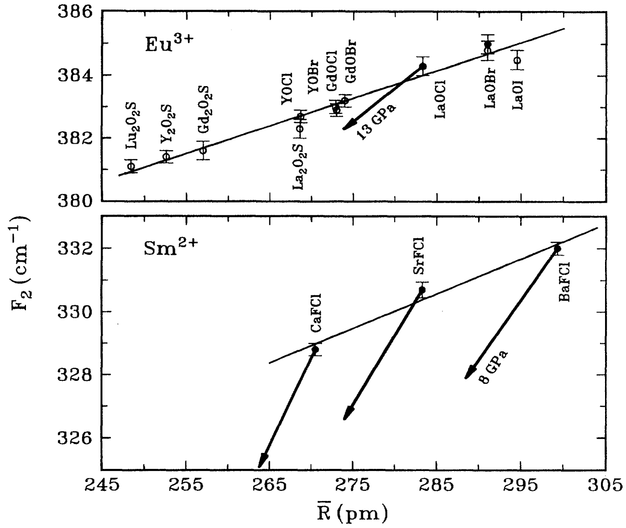

FIG. 7. Variations of the Slater parameter F_2 (cm^{-1}) for Sm^{2+} and Eu^{3+} in different host crystals as a function of $\bar{R}$ (pm). Arrows with the solid circles denote the variations under pressure.

the comparison of Eu^{3+}:L_2O_2S with Eu^{3+}:LaOI, the nephelauxetic series breaks down, because the contributions of S^{2-} and I^- ligands should be similar in magnitude according to this series. For example, the La-O distances are approximately equal in the cases of La_2O_2S and LaOI crystals, so that O^{2-} ligands should contribute the same amount to the reduction of F_2 and ζ_{4f} in both cases. Thus, the surprisingly large difference in F_2 and ζ_{4f} between Eu^{3+}:La_2O_2S and Eu^{3+}:LaOI must result from the difference of the S^{2-} and I^- ligands.

For Sm^{2+} in different MFX compounds, one has no experimental results for Sm^{2+} in MFBr or MFI to confirm this same effect. However, preliminary measurements on Sm^{2+}:BaFBr at ambient pressure and 20 K were performed in the present study to determine the positions of the ^5D_J multiplets. The observed values of 14 551 cm^{-1} for $^5D_0$ and 15 890 cm^{-1} for $^5D_1$ are both larger by 21 and 22 cm^{-1} than the corresponding values of Sm^{2+}:BaFCl and from the systematic result shown in Fig. 2 a larger Slater parameter

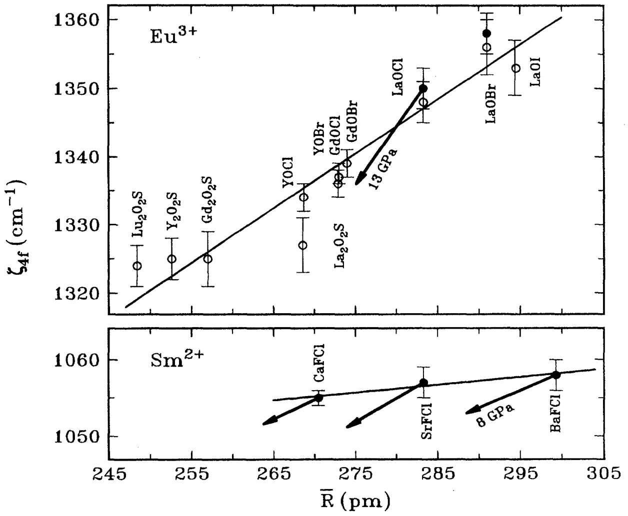

FIG. 8. Variations of the spin-orbit parameter ζ_{4f} (cm^{-1}) for Sm^{2+} and Eu^{3+} in different host crystals as a function of $\bar{R}$ (pm). Arrows with the solid circles denote the variations under pressure.

F_2 for Sm^{2+}:BaFBr is then derived also with respect to Sm^{2+}:BaFCl. Together with the known structural parameters of BaFBr,[29] which results in $\bar{R}=307.2$ pm, the larger value of F_2 for Sm^{2+}:BaFBr fits then also very well to the distance dependence of F_2 in Fig. 7, but violates the nephelauxetic series.

However, it is not clear whether the two different types of ligand ions in the present series of ternary *MYX* compounds could also result in contributions from ligand-ligand interactions which could equally well lead to a counterbalance of the different ligand types with serious deviations from the nephelauxetic series.

B. Covalency models

The $4f$ radial wave functions $R_{4f}(r)$ of free lanthanide ions are commonly described by a linear combination of a few Slater orbitals.[36] Within the two different covalency models, the open-shell $4f$ orbitals expand, when a lanthanide ion is embedded into a host. In the CFC model, this expansion is caused by a spherically symmetric penetration of ligand electrons into the $4f$ orbitals, and this expansion is then described in first order by an "expansion parameter" κ in the radial wave function

$$R_{4f}(r)=\kappa^{9/2}\sum_i C_i r^3 e^{-\kappa Z_i r}, \qquad (2)$$

where C_i and Z_i represent regular expansion coefficients and orbital exponents, respectively. In this approximation, the Slater parameters and the spin-orbit coupling parameter are related to the corresponding free-ion parameters F_2^0 and ζ_{4f}^0 just by this one parameter κ:

$$F_k=\kappa F_k^0 \quad \text{and} \quad \zeta_{4f}=\kappa^3\zeta_{4f}^0. \qquad (3)$$

In other words, such an isotropic ligand-electron penetration screens the effective nuclear charge Z_{eff} of the lanthanide ion which results in the expansion of the $4f$ orbitals and one expects then for lanthanides $F_k \sim Z_{\text{eff}}$ and $\zeta_{4f}\sim Z_{\text{eff}}^3$, which corresponds to Eq. (3) with $\kappa=Z_{\text{eff}}/Z_{\text{eff}}^0$.

Within the SRC mechanism, on the other hand, the $4f$ orbitals φ_m are modified by the symmetry-dependent covalency admixture with the ligand orbitals χ_τ and the molecular orbitals φ'_Γ are given by

$$\varphi'_\Gamma=\mathcal{N}_\Gamma\left(\varphi_\Gamma-\sum_\tau \lambda_{\Gamma\tau}\chi_\tau\right), \qquad (4)$$

with

$$\mathcal{N}_\Gamma=\left(1-2\sum_\tau \lambda_{\Gamma\tau}S_{\Gamma\tau}+\sum_\tau \lambda_{\Gamma\tau}^2\right)^{-1/2}, \qquad (5)$$

where the $\lambda_{\Gamma\tau}$'s represent admixture coefficients, which are simple sums of the overlap integrals $S_{\Gamma\tau}$ and the conventional covalency parameters $\gamma_{\Gamma\tau}$. When this covalency is weak, a good approximation for the modified $4f$ orbitals φ'_Γ in Eq. (4) is given simply by $\mathcal{N}_\Gamma\varphi_\Gamma$ with the results for the Slater parameters and the spin-orbit coupling parameter in the forms

$$F_k=\mathcal{N}^4F_k^0 \quad \text{and} \quad \zeta_{4f}=\mathcal{N}^2\zeta_{4f}^0, \qquad (6)$$

where the $\mathcal{N}_\Gamma$'s for all the different orbitals are usually assumed to be approximately equal. The reductions of the free-ion parameters in a crystal are then correlated by Eq. (6), where $\mathcal{N}$ can be treated as the one adjustable, empirical parameter.

Usually, either the CFC or SRC mechanism has been used separately to describe the nephelauxetic effect of the lanthanide ions. However, these two kinds of the mechanisms could also act simultaneously and a suitable combination of them may be used most reasonably to describe in general the lanthanide systems. In the simplest way, the radial wave function of Eq. (2) is directly used in Eq. (4), which results then in $F_k=\mathcal{N}^4\kappa F_k^0$ and $\zeta_{4f}=\mathcal{N}^2\kappa^3\zeta_{4f}^0$. Correspondingly, their relative reductions can be written as

$$\frac{\Delta F_k}{F_k}=\frac{\Delta\kappa}{\kappa}+4\frac{\Delta\mathcal{N}}{\mathcal{N}} \quad \text{and} \quad \frac{\Delta\zeta_{4f}}{\zeta_{4f}}=3\frac{\Delta\kappa}{\kappa}+2\frac{\Delta\mathcal{N}}{\mathcal{N}}. \qquad (7)$$

From the experimental data given in Figs. 7 and 8 one finds that the variation for Eu^{3+} from LaOI to Lu_2O_2S amounts to -1.04% for F_2 and -2.70% for ζ_{4f}, while $\bar{R}$ changes from 248.4 pm to 294.7 pm. Thereby, the relative reduction of $\Delta F_2/F_2$ with respect to $\Delta\zeta_{4f}/\zeta_{4f}$ is almost three times weaker, which would correspond to the prediction of the CFC model. The direct use of Eq. (7) gives for this case $\Delta\kappa/\kappa=-0.87\%$ and $\Delta\mathcal{N}/\mathcal{N}=-0.04\%$. This result indicates that the contribution from the CFC to the reduction of F_2 and ζ_{4f} dominates in the case of Eu^{3+}. Also, in the cases of Eu^{3+}:LaOCl and Eu^{3+}:LaOBr under pressures up to 13 GPa, the variations in F_2 and ζ_{4f} by -0.56% and -1.18%, respectively, deviate only slightly from the CFC model and result in changes for κ of -0.36% and $\mathcal{N}$ of -0.05%. In comparison with ambient-pressure data the contribution of the SRC becomes more significant under pressure in this case.

In the same way, the "chemical shifts" for Sm^{2+} in *M*FCl compounds at ambient pressure shown in Figs. 7 and 8 are modeled by $\Delta\kappa/\kappa=0.08\%$ and $\Delta\mathcal{N}/\mathcal{N}=-0.28\%$ and the pressure shifts for a pressure range of 8 GPa in these three hosts result just in the same values. This equivalence of chemical and pressure shifts for Sm^{2+} in *M*FCl hosts has been discussed already in relation with Figs. 3 and 4.

The small positive value for $\Delta\kappa/\kappa$ seems not to be significant within the given uncertainty of this analysis and may be considered only as an indication for the overwhelming dominance of the SRC in the case of Sm^{2+}.

Thus, one can notice that changes in the CFC or in other words changes in the shielding of the total nuclear charge represent the dominant contribution to the decrease in F_2 and ζ_{4f} for the small Eu^{3+} ion in different hosts with small contributions only from the SRC or "ligand hybridization," which increases more rapidly in this case with pressure than by chemical shifts, whereas for the larger Sm^{2+} ion this "ligand hybridization" seems to explain all the effects.

From this point of view, it is interesting to check whether this SRC model can also predict quantitatively the changes of F_2 and ζ_{4f} for Sm^{2+} ions in different surroundings with different values for the average distance $\bar{R}$.

TABLE IV. Sum values (in units of 10^{-4} a.u.) of the Coulomb integrals $\mathrm{CI}_1(m_1,m_2)$, $\mathrm{CI}_2(m_1,m_2)$, and $\mathrm{CI}_3(m_1,m_2)$ for the systems Sm^{2+}-F^- and Sm^{2+}-Cl^- at interionic distances 4.704 a.u. and 5.906 a.u., respectively, corresponding to an average distance $\bar{R}=5.372$ a.u.

	$m_1 \backslash m_2$	0	1	2	3
CI_1	0	−33.391	−19.377	−14.015	−12.590
	1	−19.377	−7.279	−3.516	−3.283
	2	−14.015	−3.516	0	0
	3	−12.590	−3.283	0	0
CI_2	0	29.265	17.619	14.455	14.251
	1	17.619	6.033	2.994	2.960
	2	14.455	2.994	0	0
	3	14.251	2.960	0	0
CI_3	0	−73.265	−41.297	−34.560	−33.548
	1	−41.297	−12.225	−5.740	−5.596
	2	−34.560	−5.740	0	0
	3	−33.548	−5.596	0	0

C. Quantitative calculations of Slater parameter variations for Sm^{2+} within the SRC model

The contributions from the orbitals χ_τ ($\tau = s$, $p\sigma$, and $p\pi$) of a ligand to the $4f$ orbitals φ_m with $m = 0, \pm 1$ of the central $4f$ ion are represented in the molecular orbital approximation by

$$\varphi_0' = \mathcal{N}_0(\varphi_0 - \lambda_{p\sigma}\chi_{p\sigma} - \lambda_s\chi_s),$$

$$\varphi_1' = \mathcal{N}_1(\varphi_1 - \lambda_{p\pi}\chi_{p\pi}),$$

$$\varphi_2' = \varphi_2,$$

$$\varphi_3' = \varphi_3.$$

With the use of the radial wave functions for Sm^{2+}, F^-, and Cl^- from the literature,[36–38] an *ab initio* calculation of the diagonal Coulomb interactions (CI's) involves only three covalency corrections $\mathrm{CI}_1(m_1,m_2)$, $\mathrm{CI}_2(m_1,m_2)$, and $\mathrm{CI}_3(m_1,m_2)$ with respect to the unperturbed $4f$ Coulomb integrals $\langle \varphi_{m_1}\varphi_{m_2}|r_{12}^{-1}|\varphi_{m_1}\varphi_{m_2}\rangle$, when only terms in λ_m and λ_m^2 are taken into account with

$$\mathrm{CI}_1(m_1,m_2) = \mathcal{N}_{m_1}^2\mathcal{N}_{m_2}^2(-2\lambda_{m_1}\langle \chi_{m_1}\varphi_{m_2}|r_{12}^{-1}|\varphi_{m_1}\varphi_{m_2}\rangle$$
$$-2\lambda_{m_2}\langle \chi_{m_2}\varphi_{m_1}|r_{12}^{-1}|\varphi_{m_2}\varphi_{m_1}\rangle),$$

$$\mathrm{CI}_2(m_1,m_2) = \mathcal{N}_{m_1}^2\mathcal{N}_{m_2}^2(\lambda_{m_1}^2\langle \chi_{m_1}\varphi_{m_2}|r_{12}^{-1}|\chi_{m_1}\varphi_{m_2}\rangle$$
$$+\lambda_{m_2}^2\langle \chi_{m_2}\varphi_{m_1}|r_{12}^{-1}|\chi_{m_2}\varphi_{m_1}\rangle),$$

$$\mathrm{CI}_3(m_1,m_2) = (\mathcal{N}_{m_1}^2\mathcal{N}_{m_2}^2 - 1)\langle \varphi_{m_1}\varphi_{m_2}|r_{12}^{-1}|\varphi_{m_1}\varphi_{m_2}\rangle.$$

In addition to the two-center integrals for the ion pairs $\mathrm{Sm}^{2+}(4f)$-$\mathrm{F}^-(2s,2p)$ and $\mathrm{Sm}^{2+}(4f)$-$\mathrm{Cl}^-(3s,3p)$ also the corresponding overlap integrals have to be calculated for the evaluation of the renormalization parameters $\mathcal{N}$ as given in Eq. (5). With the admixture coefficients λ from the literature[20] and the known interionic distances for Sm^{2+} in SrFCl at ambient pressure, numerical calculations result in the data given in Table IV. With these results, the reductions $\delta F_k = F_k - F_k^0$ of the free-ion Slater parameters F_k^0 are calculated first for the two different ligands and then added up according to the given coordination numbers in the evaluation of the total effects for Sm^{2+}:SrFCl: $\delta F_2 = -2.4\ \mathrm{cm}^{-1}$, $\delta F_4 = -0.65\ \mathrm{cm}^{-1}$, and $\delta F_6 = -0.11\ \mathrm{cm}^{-1}$.

TABLE V. Overlap integrals ($\times 10^{-2}$) of Eu^{3+}-O^{2-} and Eu^{3+}-Cl^- ion pairs at different distances R (a.u.), corresponding to the values of LaOCl at ambient pressure and 13 GPa. S_Σ denotes a sum of S_s, $S_{p\sigma}$, and $S_{p\pi}$. The radial wave functions of Eu^{3+}, O^{2-}, and Cl^- are employed here in Refs. 42, 43, and 38.

	R	S_s	$S_{p\sigma}$	$S_{p\pi}$	S_Σ
Eu^{3+}-O^{2-}	4.511	1.284	1.545	1.064	3.893
	4.405	1.434	1.672	1.184	4.290
Eu^{3+}-Cl^-	6.057	0.340	0.684	0.369	1.393
	5.907	0.401	0.762	0.423	1.586
	5.860	0.422	0.788	0.442	1.652
	5.732	0.489	0.870	0.501	1.860

Thereby, one can notice that opposite signs of the contributions from $\mathrm{CI}_1(m_1,m_2)$ and $\mathrm{CI}_2(m_1,m_2)$ shown in Table IV lead to a strong cancellation of these terms as noticed previously[10] for the system Pr^{3+}-Cl^-. Due to this cancellation, one finds that the simple replacement of the covalency-modified $4f$ orbitals φ'_Γ by $\mathcal{N}_\Gamma\varphi_\Gamma$ results already in a reasonable approximation with typical errors for δF_2 of about 20% and the same approximation for the renormalization parameter $\mathcal{N}$ of the different admixture orbitals leads only to the error less than 0.5%.

Experimental data for F_k^0 of the free ion Sm^{2+}, called Sm(III), are not available for a direct comparison with the present calculation; however, the parameters F_2 and ζ_{4f} for the free ion Sm(I) with a ground electron configuration $4f^66s^2$ have been determined experimentally:[39] $F_2 = 335.6\ \mathrm{cm}^{-1}$ and $\zeta_{4f} = 1062\ \mathrm{cm}^{-1}$. Since the energy levels of the $4f^n$ core are almost independent of the number of outer $6s$ electrons in the lanthanide series,[6] one can safely assume that the free-ion parameters for Sm(III) have the same values as for Sm(I), and this assumption is further supported by the almost identical energy level schemes for the free ions Sm(III) (Ref. 40) and Sm(I).[39] With these results, one obtains a reduction of F_2 for Sm^{2+} in SrFCl of about $4.9\ \mathrm{cm}^{-1}$, whereas the present calculation gives a value of $2.4\ \mathrm{cm}^{-1}$, which is considered as good agreement.

The Slater parameters F_k evaluated by the use of the Hartree-Fock $4f$ radial wave functions[36] are considerably larger than the observed values for the lanthanide ions, since the Hartree-Fock wave functions are too much contracted due to an omission of configuration interactions, and configuration mixing of the $4f^n$ configuration with other configurations up to 50% is well known.[41] This discrepancy can be removed, however, by an artificial expansion of the Hartree-Fock $4f$ radial wave functions to simulate configuration mixing.

In the same way, one can also estimate the contributions of the covalency admixture to the parameter reductions for Eu^{3+} ions. For example, Table V gives the overlap integrals S_s, $S_{p\sigma}$, and $S_{p\pi}$ of Eu^{3+}-O^{2-} and Eu^{3+}-Cl^- ion pairs for Eu^{3+}:LaOCl at ambient pressure and 13 GPa. In the evaluation of the renormalization constants $\mathcal{N}$, one can reasonably assume the ratio between the total admixture coefficient λ_Σ and the total overlap integral S_Σ of the s, $p\sigma$, and $p\pi$ orbitals $\lambda_\Sigma/S_\Sigma \approx 2.2$ for Eu^{3+}-O^{2-} and Eu^{3+}-Cl^- ion pairs according to *ab initio* calculations for Pr^{3+}-Cl^- (Ref. 44) and Pr^{3+}-F^- ion-pairs.[45] The change in $\mathcal{N}$ from all the nine ligand ions under pressures up to 13 GPa is found to amount then to about -0.04% which is in very close agreement with the "experimental" value of -0.05% derived in the previous section.

V. CONCLUSIONS

The comparison of "chemically" and pressure-induced changes in the Slater parameter F_2 and in the spin-orbit coupling parameter ζ_{4f} for the $4f$ electrons of Sm^{2+} and Eu^{3+} ions in different host materials results in the following conclusions.

(i) The nephelauxetic series breaks down in ternary compounds, at least in the cases of Sm^{2+} and Eu^{3+} in the present hosts.

(ii) The reduction of the parameters F_2 and ζ_{4f} is caused in general by two different covalency contributions, the central-field covalency or "central-charge screening" and the symmetry-restricted covalency or "ligand hybridization." From a comparison of the relative decrease in F_2 and ζ_{4f} one can find out which of these two mechanisms is more dominant.

(iii) For small, trivalent lanthanide ions, like Eu^{3+}, the "central-charge screening" is dominant, whereas the "ligand hybridization" is the dominant mechanism in larger, divalent lanthanide ions like Sm^{2+}.

(iv) *Ab initio* calculations of the decrease in F_k for Sm^{2+} agree quantitatively with the experimental results within the mutual uncertainties of 10% of the changes.

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